

REPORT DOCUMENTATION PAGE					Form Approved OMB No. 0704-0188	
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to the Department of Defense, Executive Services and Communications Directorate (0704-0188). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.</p>						
1. REPORT DATE (DD-MM-YYYY) 07-06-2006		2. REPORT TYPE Journal Article (refereed)			3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Evaluation of Deoxygenation as a Corrosion Control Measure for Ballast Tanks				5a. CONTRACT NUMBER		
				5b. GRANT NUMBER		
				5c. PROGRAM ELEMENT NUMBER PE0601153N		
6. AUTHOR(S) Jason S. Lee, Richard I. Ray, Brenda J. Little, Edward Lemieux				5d. PROJECT NUMBER		
				5e. TASK NUMBER		
				5f. WORK UNIT NUMBER 73-5052-14-5		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Research Laboratory Oceanography Division Stennis Space Center, MS 39529-5004					8. PERFORMING ORGANIZATION REPORT NUMBER NRL/JA/7303-05-5135	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy St. Arlington, VA 22217-5660					10. SPONSOR/MONITOR'S ACRONYM(S) ONR	
					11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution is unlimited.						
13. SUPPLEMENTARY NOTES						
14. ABSTRACT Field experiments designed to evaluate deoxygenation of natural seawater as a corrosion control measure for unprotected carbon steel seawater ballast tanks demonstrated decreased corrosion in hypoxic (<0.2 ppm O ₂) seawater using linear polarization measurements. They also demonstrated the difficulty of maintaining hypoxic seawater. Using a gas mixture it was possible to displace dissolved oxygen. However, aerobic respiration and corrosion reactions consumed oxygen and produced totally anaerobic conditions within the first days of hypoxia. When gaskets and seals failed, oxygen was inadvertently introduced. The impact of oxygen ingress on corrosion depends on the amount of oxygen in the system at the time oxygen is introduced. Carbon steel exposed to cycles of hypoxic seawater and oxygenated atmosphere had higher corrosion rates than coupons exposed to cycles of either consistently aerobic or deoxygenated conditions.						
15. SUBJECT TERMS alternate immersion, ballast, carbon steel, deoxygenation, seawater						
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UL	18. NUMBER OF PAGES 16	19a. NAME OF RESPONSIBLE PERSON Jason S. Lee	
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code) (228) 688-4494	

Evaluation of Deoxygenation as a Corrosion Control Measure for Ballast Tanks

J.S. Lee,^{†*} R.I. Ray,^{*} B.J. Little,^{*} and E.J. Lemieux^{**}

20060619022

ABSTRACT

Field experiments designed to evaluate deoxygenation of natural seawater as a corrosion control measure for unprotected carbon steel seawater ballast tanks demonstrated decreased corrosion in hypoxic (<0.2 ppm O₂) seawater using linear polarization measurements. They also demonstrated the difficulty of maintaining hypoxic seawater. Using a gas mixture it was possible to displace dissolved oxygen. However, aerobic respiration and corrosion reactions consumed oxygen and produced totally anaerobic conditions within the first days of hypoxia. When gaskets and seals failed, oxygen was inadvertently introduced. The impact of oxygen ingress on corrosion depends on the amount of oxygen in the system at the time oxygen is introduced. Carbon steel exposed to cycles of hypoxic seawater and oxygenated atmosphere had higher corrosion rates than coupons exposed to cycles of either consistently aerobic or deoxygenated conditions.

KEY WORDS: alternate immersion, ballast, carbon steel, deoxygenation, seawater

INTRODUCTION

The deoxygenation of seawater has been demonstrated as an environmentally friendly ballast water treatment to control the introduction of nonnative aquatic species.¹ Investigators have proposed that the

same treatment provides a low-cost, effective corrosion control measure for uncoated carbon steel ballast tanks based on the concept that reducing oxygen from the ballast tanks will limit oxidation.¹⁻² Matsuda, et al.,² conducted shipboard trials by sealing a ballast tank at the deck and installing vertical pipes into the headspace. They reported that pumping pure nitrogen gas into the headspace for 1.5 h reduced oxygen levels in the seawater to approximately 0.2 ppm and decreased the rate of uniform corrosion of carbon steel by 90% as determined by weight loss.

Previous laboratory experiments³⁻⁴ comparing corrosion resulting from stagnant aerobic natural seawater with corrosion resulting from stagnant anaerobic natural seawater over a 1-year period demonstrated the following:

- Corrosion was more aggressive under totally anaerobic conditions as measured by instantaneous corrosion rates ($1/R_p$) and weight loss.
- Under aerobic conditions corrosion was uniform and the surface was covered with hydrous iron oxides (lepidocrocite [γ -FeO(OH)] and goethite [α -FeO(OH)]).
- Under anaerobic conditions the corrosion was localized pitting and the corrosion products were an iron/nickel sulfide (mackinawite [(Fe,Ni)S] and an iron sulfide (pyrrhotite [Fe_{1-x}S])).

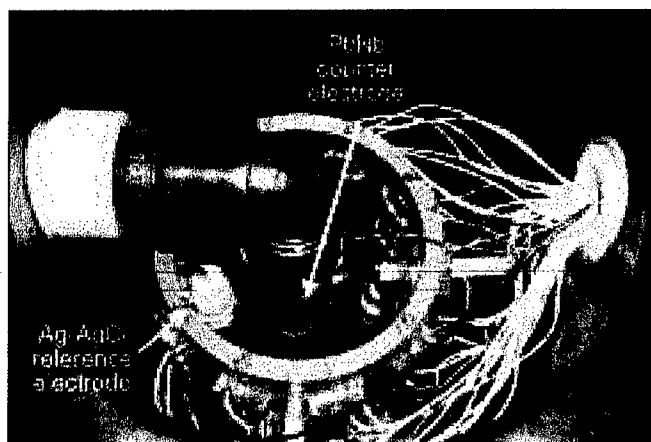
Several investigators⁵⁻⁷ have suggested that the most corrosive operating condition is one in which carbon steel is exposed to alternating oxygenated/deoxygenated seawater. Under constant oxygenation an oxide will form that provides corrosion resistance.

Submitted for publication February 2005; in revised form, May 2005. Presented as paper no. 05217 at CORROSION/2005, April 2005, Houston, TX.

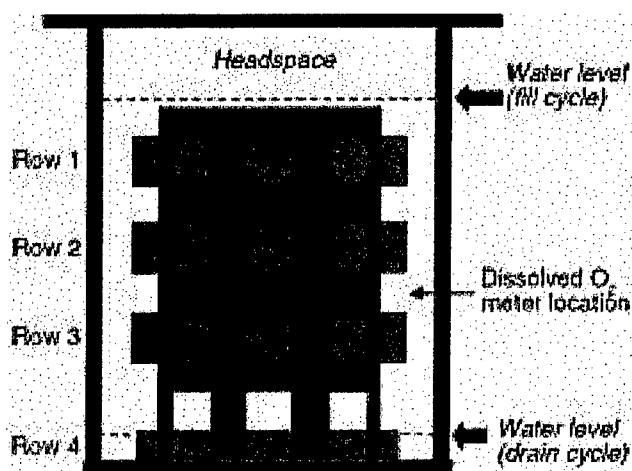
[†] Corresponding author. E-mail: jlee@nrlssc.navy.mil.

^{*} Naval Research Laboratory, Code 7330, Bldg. 1009, Rm. B131, Stennis Space Center, MS 39529.

^{**} Naval Research Laboratory, Key West, FL 33041.



(a)



(b)

FIGURE 1. (a) Experimental tank used to examine rates and mechanism of corrosion under deoxygenated conditions. (b) Schematic of coupon holder and individual side rows 1 through 3 and bottom row 4.

Under anaerobic conditions, naturally occurring sulfate-reducing bacteria (SRB) produce sulfides, resulting in the conversion of the oxide to a sulfide. The result of repeated oxygenated/deoxygenated cycles is reportedly severe localized corrosion, i.e., pitting. Most reported cases of SRB-induced corrosion of carbon steel in marine waters are in environments with some dissolved oxygen in the bulk medium.⁸ Anaerobic conditions and sulfides can form within marine biofilms at biofilm/metal interfaces, independent of bulk oxygen concentrations.⁹

Field experiments were designed to evaluate deoxygenation as a corrosion control measure for uncoated carbon steel ballast tanks exposed to natural seawater when tanks were maintained with cycles of potential operating conditions: oxygenated seawater followed by an oxygenated atmosphere, deoxygenated

TABLE 1
Chemical Composition of Carbon Steel 1020

AISI-SAE Designation	C	Mn	P max	S max	Fe
1020	0.17 to 0.23	0.3 to 0.6	0.04	0.05	Balance

seawater followed with an oxygenated atmosphere, and deoxygenated seawater followed with an inert atmosphere. Results are compared with the previously reported results for carbon steel exposed in the laboratory to stagnant aerobic and totally anaerobic natural seawater.⁴ The field experiments described in this paper were not designed to produce totally anaerobic conditions, but were meant to approximate the level of oxygen described in the Matsuda, et al., experiments,² i.e., 0.2 ppm. An important difference between this field experiment and the work reported by Matsuda is the method of deoxygenation. In the Matsuda experiment, only the atmospheric headspace was deoxygenated whereas in this field experiment, the in-flowing seawater was directly deoxygenated.

EXPERIMENTAL PROCEDURES

Three cylindrical tanks (35.5 cm diameter and 27.9 cm height) made from heavy gage, chemical-resistant, opaque polyethylene were built to expose 1020 carbon steel (UNS G10200)⁽¹⁾ to natural seawater (Figure 1[a]). Corrosion coupons were 1020 carbon steel (Table 1), 1.5 cm diameter by 0.16 cm thick with an as-mill finish. Individual insulated wires were attached to the back of each sample and held in place using conductive silver adhesive and carbon tape. The exposure side of the coupon was coated with vacuum grease and centered face down inside an epoxy mount (3.175 cm diameter by 2.54 cm high) with the wire connection exposed. Epoxy was added, covering the connection, and allowed to cure for 24 h. Vacuum grease prevented epoxy intrusion between the sample face and mount bottom, preserving the as-mill finish. Epoxy-mounted carbon steel coupons were oriented in vertical rows 1 through 3 (27 samples) and horizontal row 4 (9 samples) to simulate tank side-walls and bottoms, respectively (Figure 1[b]). Prior to seawater exposure, coupons were rinsed in acetone (CH_3COCH_3), ethanol ($\text{C}_2\text{H}_5\text{O}$), and distilled water and dried with nitrogen gas to remove vacuum grease and residual surface debris. A silver/silver chloride (Ag/AgCl) electrode and a platinum/niobium (Pt/Nb) mesh were used as reference and counter electrodes, respectively.

Experiments were conducted with natural seawater at the Naval Research Corrosion Laboratory, Key West, Florida. Coupons in the tanks were exposed to the following:

- fill/drain cycles of alternating natural oxygenated seawater and air (aerobic/aerobic)

⁽¹⁾ UNS numbers are listed in *Metals and Alloys in the Unified Numbering System*, published by the Society of Automotive Engineers (SAE International) and cosponsored by ASTM International.

TABLE 2
Seawater Chemistry

Water Condition	pH	Sulfide (ppm)	Dissolved Oxygen (ppm)	Salinity	Temperature (°C)
Raw seawater	8.02	<0.03	6.5	38	28
Deoxygenated seawater	6.23	<0.03	<0.1	38	28

TABLE 3
Physical Water Chemistry and Bacteria Counts after 14 Days of Wet Cycle for all Tanks (Collected on Day 98)

Exposure (Fill/Drain Cycle)	pH	Sulfide (ppm)	Aerobes (10) ^x	Anaerobes (10) ^x	APB (10) ^x	SRB (10) ^x
Raw seawater	8.02	<0.03	4	3	4	0
Aerobic/aerobic	7.42	0.12	1	2	2	5
Deoxygenated/aerobic	7.29	0.18	3	3	3	0
Deoxygenated/deoxygenated	6.57	0.20	3	1	2	3

- fill/drain cycles alternating deoxygenated natural seawater and air (deoxygenated/aerobic)
- fill/drain cycles alternating deoxygenated natural seawater and inert gas (deoxygenated/deoxygenated)

Natural seawater was deoxygenated using an in-line injection of premixed inert gases. A combination of carbon dioxide (CO₂) and nitrogen gases was used to decrease gas bubble size, thereby increasing the bubble surface-to-volume ratio and facilitating deoxygenation. The system was designed so that the inert gas was also used to blanket the headspace in the deoxygenated/deoxygenated exposure during the fill cycle or the entire ballast tank during the drain cycle, whereas in the deoxygenated/aerobic exposure, no attempt was made to prevent air from entering the headspace. After draining, a thin layer of seawater remained in the bottom of all tanks.

The following parameters were measured before/after deoxygenation and at 98 days' exposure: dissolved oxygen, salinity, temperature, bulk pH, and sulfide. A 20-mL water sample was removed from each tank. Sulfide concentrations were determined in triplicate using the methylene blue method¹⁰ and a spectrophotometer by extracting 1 mL and diluting 1:10 with double-distilled water. On Day 98, after 14 days of a fill cycle, a sterile 5-mL syringe was used to remove 4 mL from the 20-mL aliquot. One mL was used to inoculate serial dilutions (10⁵) of each of the following seawater media: phenol red dextrose broth, Postgate medium B, nutrient broth, and thioglycollate medium were used to determine the most probable numbers of acid-producing bacteria (APB), SRB, and general heterotrophic aerobes and anaerobes, respectively. Dilutions were incubated for 28 days at room temperature.

Four coupons (one horizontally and three vertically oriented, i.e., one from each row) were periodically (1 month to 3 months) removed. Coupons were

fixed in 4% glutaraldehyde (C₅H₈O₂) in seawater and rinsed in distilled water. Environmental scanning electron microscopy (ESEM) and energy-dispersive spectroscopy (EDS) were used to characterize corrosion morphology, biofilm structure, and corrosion products. X-ray diffraction (XRD) was used to determine the mineralogy of the corrosion products. The open-circuit potential (E_{corr} vs. Ag/AgCl) was monitored continuously using a data logger, and the linear polarization resistance method (LPR) was performed on each sample every 30 days to 90 days to obtain polarization resistance (R_p). Dissolved oxygen (DO) in each container was monitored continuously using a DO probe immersed in the midsection of the tank between rows 2 and 3, with the water level just above row 1 (Figure 1[b]).

RESULTS

Natural Key West, Florida, seawater had a pH of 8.02 while the deoxygenated seawater had a pH of 6.23. The drop in pH was due to CO₂ in the deoxygenation gas mixture. The sulfide concentration was negligible (ppb) in the natural and deoxygenated seawaters. Deoxygenation resulted in the removal of DO from the raw seawater level of 6.5 ppm to less than 0.1 ppm (Table 2). The natural seawater had high concentrations of aerobes, general anaerobes, and APB, but no culturable SRB (Table 3). Water was also analyzed after a 14-day wet cycle during the exposure period of 74 days to 98 days (Table 3). The pH fluctuated within narrow ranges from the original values. Bulk sulfide concentrations in all tanks increased (Table 3). SRB were cultured from both aerobic/aerobic and deoxygenated/deoxygenated tanks.

DO concentrations in the deoxygenated water and atmosphere were consistently higher than the design value of 0.2 ppm (Figure 2). Draining water from the tanks had a profound influence on E_{corr} measurements

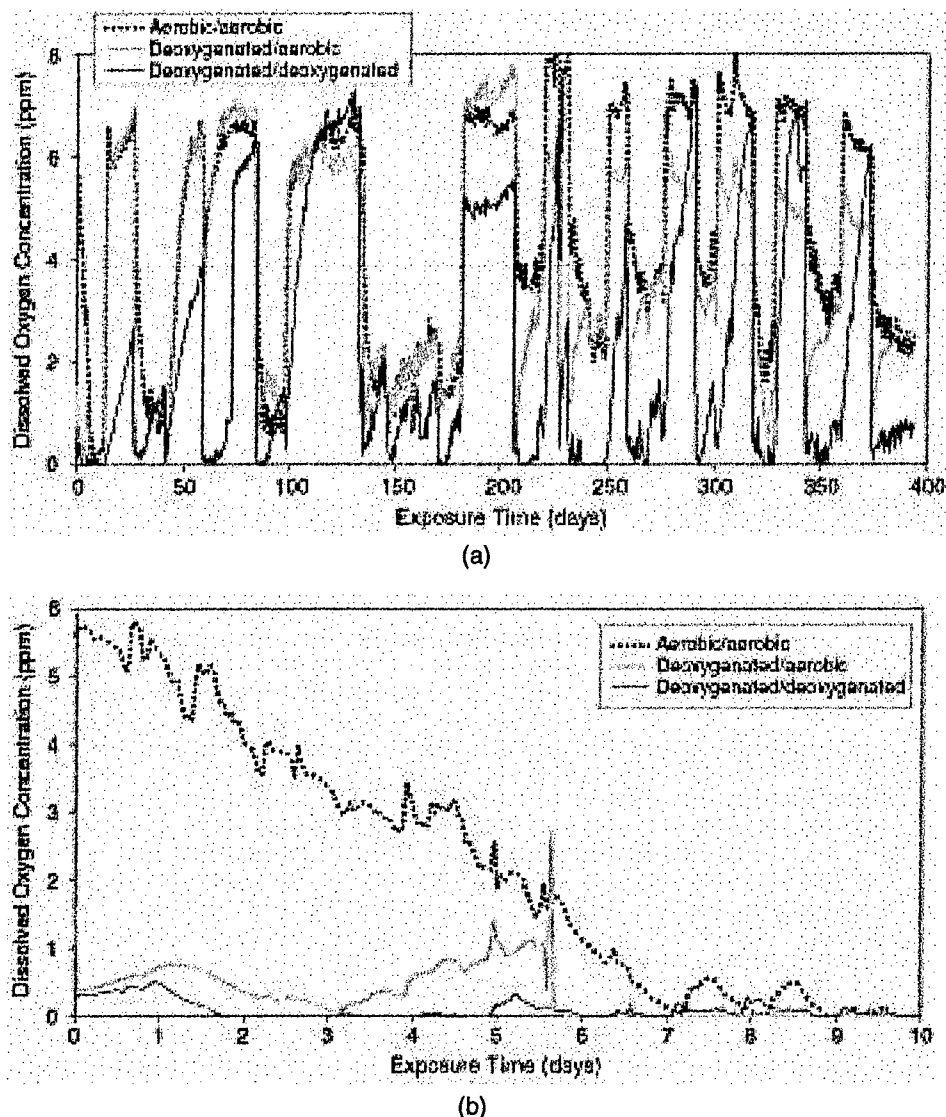


FIGURE 2. (a) Dissolved oxygen (ppm) measured in the three different exposures (fill/drain cycle condition) over the entire 395-day exposure period and (b) a close up of the first 10 days of exposure.

(Figures 3 and 4) during the first 100 days because of an incomplete circuit in the absence of the electrolyte. However, after 100 days of exposure, a sodium chloride (NaCl)-rich water film provided a salt bridge between carbon steel samples and the reference electrode, facilitating stable E_{corr} measurements during the drain cycles. Figure 4 plots E_{corr} measurements from Figure 3 sorted by row. E_{corr} values for the bottom row 4 coupons tended to be consistently low and unaffected by the fill/drain cycles, especially in the deoxygenated/deoxygenated tank (Figure 4[c]).

The specific appearance of the coupons varied with oxygen concentration in the water or atmosphere at the time of collection (Figure 5). In general all exposure conditions produced a two-tiered corrosion layer. In the presence of oxygen, the outer, extremely fragile layer was reddish orange and XRD data indicated halite (NaCl), lepidocrocite, and goethite. The inner

layer was black, tenacious, and XRD indicated magnetite ($\gamma\text{-Fe}_2\text{O}_3$). Images in Figure 5 represent a single row of coupons (row 2) collected at 98, 146, 237, and 395 days from the deoxygenated/deoxygenated tank. Images in Figure 6 demonstrate differences between side and bottom coupons. All outer layers contained concentrations of twisted bacterial filaments that, in some cases, were encrusted in iron (Figure 7). EDS spectra indicated minor amounts of sulfur in corrosion products on all coupons. Trace amounts of mackinawite were identified by XRD in the corrosion products formed under deoxygenated/deoxygenated conditions. The appearance of the coupons gave no indications of the type, severity, or distribution of the corrosion (Figure 8). Coupons removed from side row 1 (Figure 8[b]) were pitted over roughly one-half of the surface. Corrosion on the coupon exposed in bottom row 4 was general over the entire surface (Figure 8[d]).

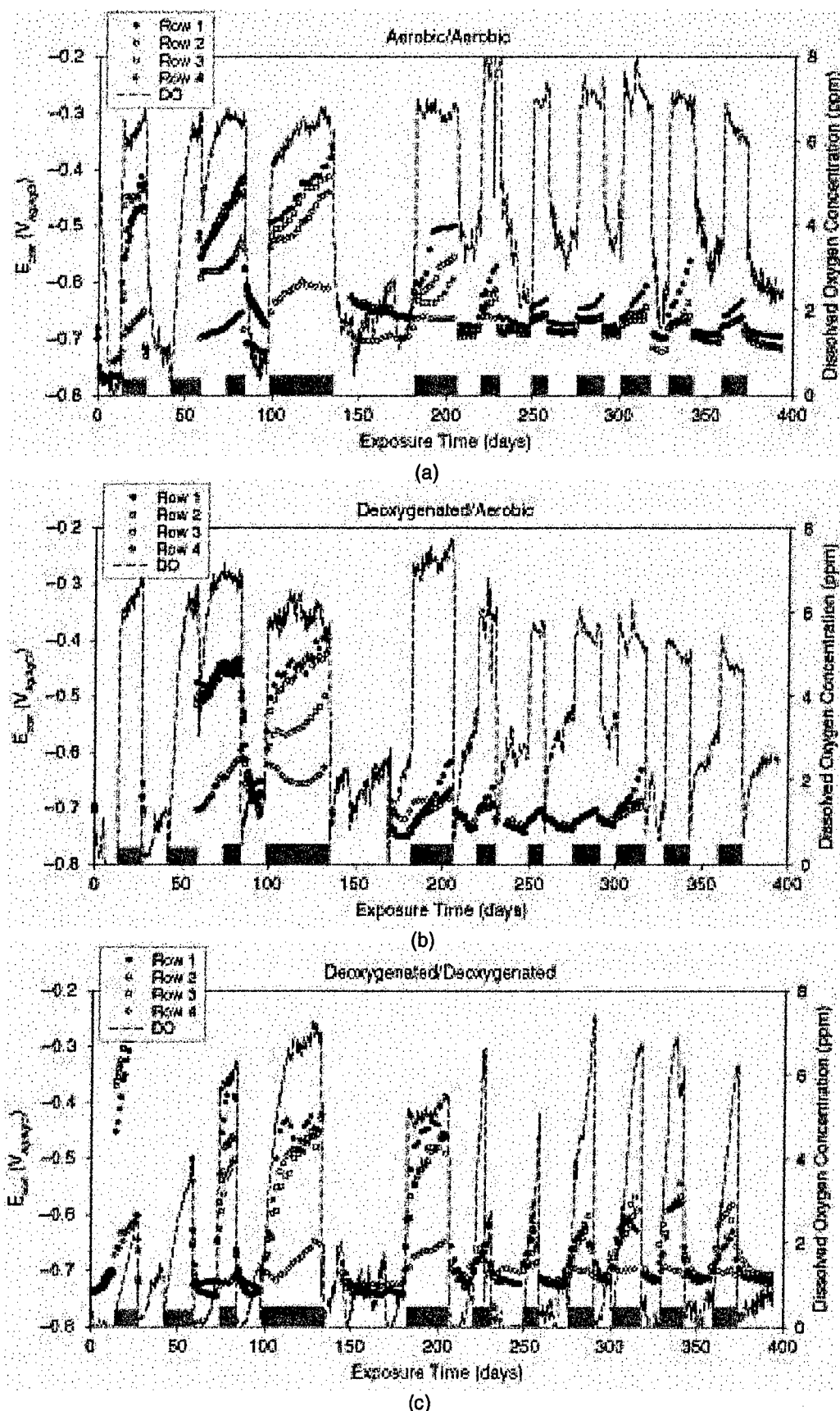


FIGURE 3. Average E_{corr} (V_{Ag/AgCl}) values for the four coupon rows for fill/drain exposure conditions: (a) aerobic/aerobic, (b) deoxygenated/aerobic, and (c) deoxygenated/deoxygenated. Dissolved oxygen levels (ppm) are plotted on the secondary y-axis with shaded areas indicating drain cycle periods.

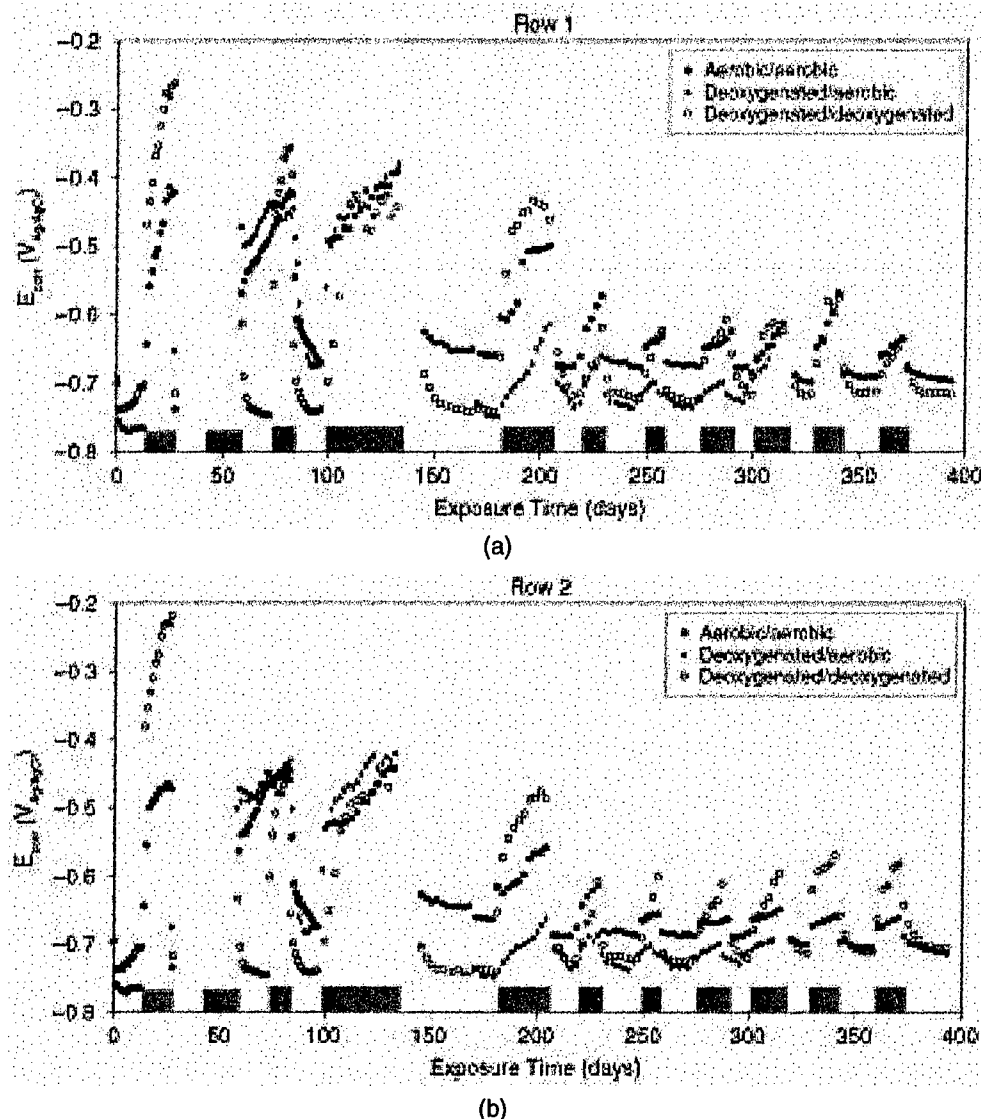


FIGURE 4. Average E_{corr} ($V_{Ag/AgCl}$) values for the three fill/drain exposure conditions sorted by coupon row: (a) row 1, (b) row 2, (c) row 3, and (d) row 4. Shaded areas indicate drain cycle periods.

Instantaneous corrosion rates ($1/R_p$ reported in units of Ω^{-1}) were measured using the LPR technique every 30 days to 90 days and are reported as average values in Figures 9 and 10 sorted by tank and row, respectively. The $1/R_p$ data for the aerobic/aerobic tank (Figure 9[a]) indicated side rows 1 through 3 corroded at rates 1.5 to 3 times faster than bottom row 4 over the first 170 days. Corrosion rates for side row coupons were very dynamic in comparison to the stable rates for the bottom row samples. For example, the side rows showed the largest range ($0.0015 \Omega^{-1}$ to $0.013 \Omega^{-1}$) of rates over the experimental period time, while those of the bottom row had a much smaller range ($0.0015 \Omega^{-1}$ to $0.006 \Omega^{-1}$). The $1/R_p$ data for the deoxygenate/aerobic tank (Figure 9[b]) indicated that, initially, side row coupons corroded faster than bottom row coupons. However, at 98 days the bottom row began to corrode slightly faster than the side rows. At

137 days, the corrosion rate for the side rows increased to $0.022 \Omega^{-1}$ while the corrosion rate for the bottom row was around $0.005 \Omega^{-1}$. This jump in corrosion rates for side row coupons corresponded to measurements taken immediately after a long (~47 days) empty cycle with 7 ppm oxygen in the atmosphere (Figure 2[a]). Corrosion rates for side row coupons during this period were twice as high as the largest corrosion rate measured for any row in the aerobic/aerobic tank for the entire exposure. For the remainder of the experiment, the bottom row corroded at twice the rate of the side rows. At 395 days, the bottom row corrosion rate increased to the high rate ($0.022 \Omega^{-1}$), observed at 137 days for the side rows. The $1/R_p$ data for the deoxygenated/deoxygenated tank (Figure 9[c]) followed the same trends for the first 170 days as that of the deoxygenated/aerobic tank, including a jump ($0.012 \Omega^{-1}$) in corrosion rates for the

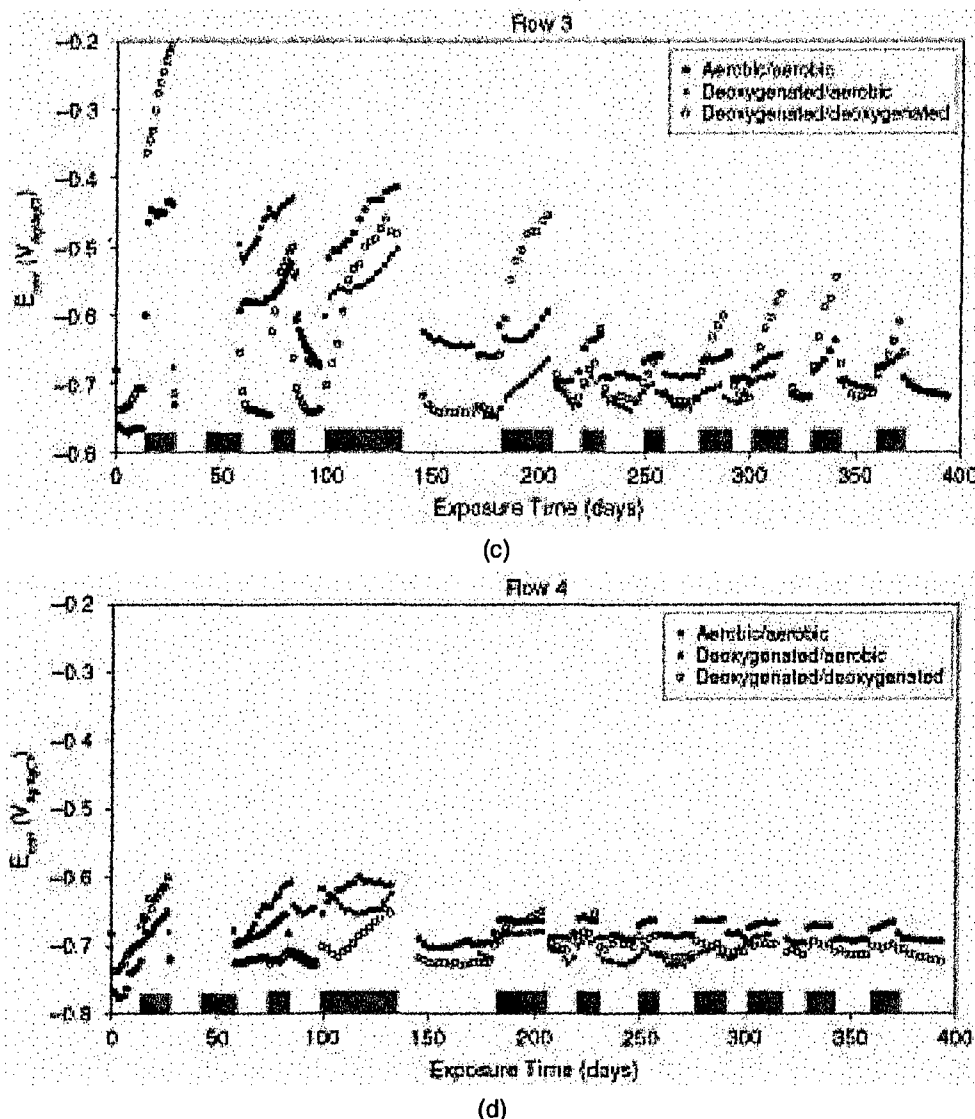


FIGURE 4 (continued). Average E_{corr} ($V_{\text{Ag/AgCl}}$) values for the three fill/drain exposure conditions sorted by coupon row: (a) row 1, (b) row 2, (c) row 3, and (d) row 4. Shaded areas indicate drain cycle periods.

side row samples at 137 days. At 170 days, all rows had the same low corrosion rate of $0.001 \Omega^{-1}$. However, at 207 days, corrosion rates of all rows increased to between $0.007 \Omega^{-1}$ to $0.01 \Omega^{-1}$ with row 1 having the highest and row 4 having the lowest rate. This rate increase corresponded to a measurement taken after a 46-day exposure to 5 ppm atmospheric oxygen. Interestingly, coupons in the aerobic/aerobic and deoxygenated/aerobic tanks were exposed to higher concentrations of atmospheric oxygen (7 ppm) over the same exposure period but did not exhibit the same increase in corrosion rates as the side row coupons in the deoxygenated/deoxygenated tank. After 207 days, corrosion rates of the side rows remained low at $0.001 \Omega^{-1}$ while the bottom row corroded at twice the rate but was still low in comparison to the deoxygenated/aerobic tank. Figure 10 plots corrosion rate data from Figure 9 sorted by row. Side rows 1, 2,

and 3 all have the same corrosion behavior for a given tank. Corrosion rates were highest for the side row coupons in the deoxygenated/aerobic tank. Corrosion rates for the side rows in the aerobic/aerobic tank were unaffected by long periods of exposure to atmospheric oxygen, whereas the side rows in the other two tanks were strongly affected in the first 150 days, after which only the deoxygenated/aerobic tank was consistently affected by atmospheric oxygen levels. The $1/R_p$ values for row 4 of all tanks were low initially. The instantaneous corrosion rate for row 4 of the aerobic/aerobic tank remained stable throughout the experiment as did those in the deoxygenated/deoxygenated tank. At the conclusion of the experiment, coupons in row 4 of the deoxygenated/aerobic tank were corroding at the highest rate of any of the rows in any of the tanks. Figure 11 is the combined data of all tanks and rows with the side rows reported

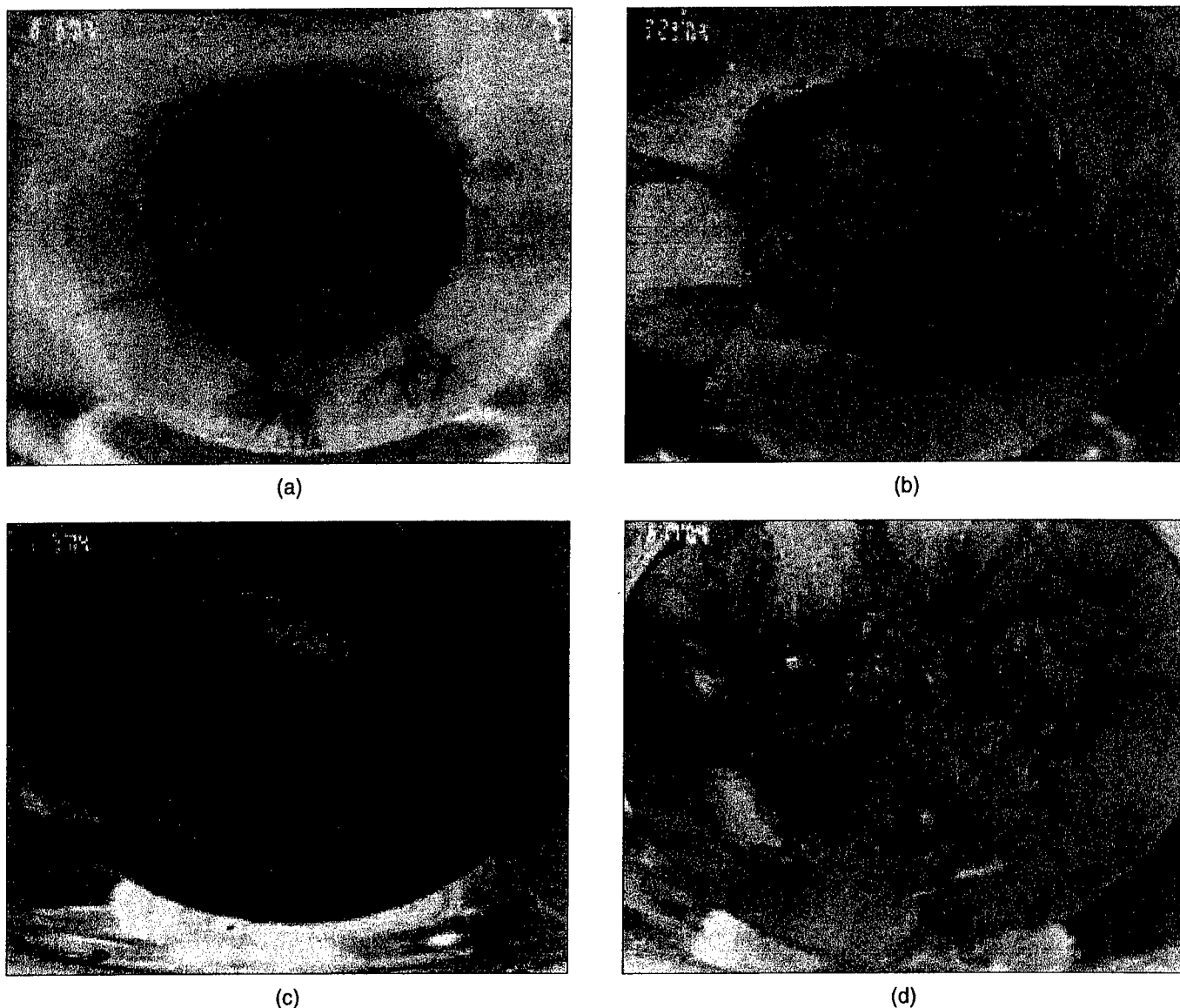


FIGURE 5. Photographs of row 2 coupons from deoxygenated/deoxygenated fill/drain condition after exposure times of (a) 98, (b) 146, (c) 237, and (d) 395 days.

as an average. Coupons in the deoxygenated/oxygenated tank row 4 had the highest corrosion rates over the experiment, while the side rows in the aerobic/aerobic tank and all coupons in the deoxygenated/deoxygenated tank had the lowest. Weight-loss data indicate the same trends (data not shown).

DISCUSSION

Dissolved oxygen levels were decreased to hypoxic levels by the direct treatment of raw seawater with an inert gas mixture and dissolved oxygen levels were measured within the water column itself. In contrast, Matsuda, et al.,² pumped nitrogen gas only into the headspace of a partially filled, sealed ballast tank for 1.5 h. They placed an oxygen sensor in the headspace and deduced that the purge gas equilibrated with the

dissolved gases in the water column to produce a DO concentration of approximately 0.2 ppm. DO concentration in the water was not measured. They indicated that controlling the oxygen concentration in their shipboard experiments was the most difficult aspect of their deoxygenation experiment. The oxygen data from the field experiment reported in this paper (Figure 2) demonstrate that difficulty. In the initial stages (Figure 2[b]) of the experiment, it is extremely easy to reduce the oxygen concentration in the bulk seawater to below 1 ppm. However, aerobic respiration and abiotic corrosion reactions consume oxygen readily and drive the DO concentration to zero within days in all tanks resulting in anaerobic conditions. Maintaining a specific hypoxic DO concentration in a sealed tank will require an accurate prediction of probable oxygen consumption, monitoring, and the

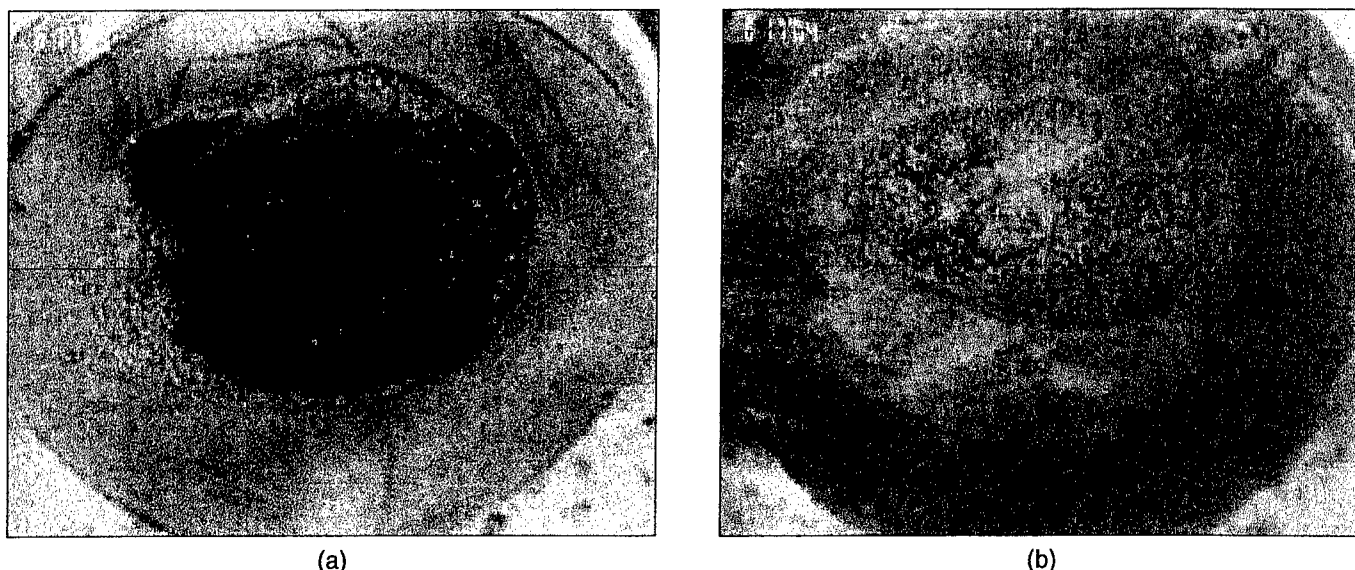
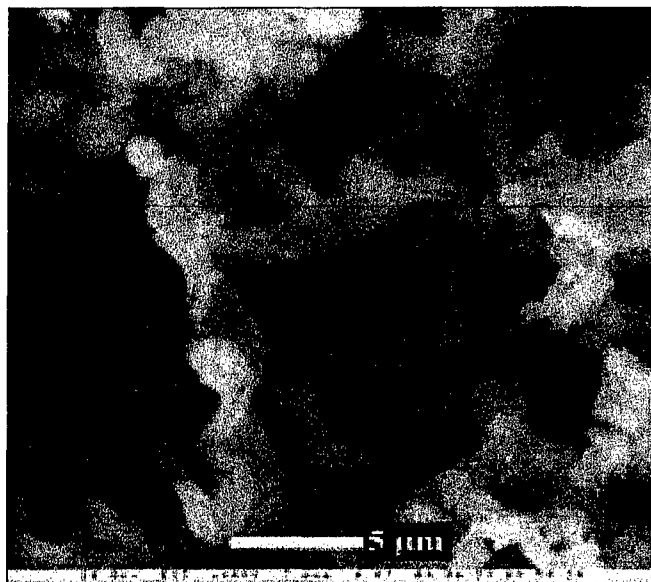


FIGURE 6. Photographs indicating the different appearance of (a) row 1 and (b) row 4 coupons from deoxygenated/aerobic fill/drain condition after 395 days' exposure.

ability to add oxygen should respiration and corrosion reactions reduce DO below the target concentration. The concentration of DO in the seawater was a direct function of the performance of the gaskets and seals. When the seals held it was possible to maintain the decreased oxygen levels in the water. When seals failed (e.g., 100 days and 180 days), oxygen diffused into the tanks immediately. While we were unable to maintain the desired hypoxic conditions in the seawater and atmosphere, we can assess the corrosion of carbon steel resulting from the ingress of the oxygen into the hypoxic environments. Peaks in the instantaneous corrosion rates at 137 days and 207 days (Figure 9) followed periods of exposure to atmospheric oxygen (Figure 2[a]). Corrosion rates of side row coupons of the two exposure conditions with deoxygenated seawater (deoxygenated/aerobic and deoxygenated/deoxygenated) were affected. Bottom rows were less affected because the residual water prevented desiccation. Hypoxic conditions in the deoxygenated/deoxygenated tank produced the desired effect of reducing corrosion as measured by LPR. However, the introduction of oxygen caused an immediate increase in the corrosion rate. These results confirm the experiments of Hardy and Bown⁵ and Lee and coworkers.⁶⁻⁷

Our data demonstrate an important practical consideration not previously discussed by other authors. The increase in the instantaneous corrosion rate does not correspond directly with the amount of oxygen introduced at any one time. Instead the increase is related to the prevailing oxygen concentration at the time oxygen is introduced. At the time of inadvertent oxygen introduction, the lower the concentration of dissolved oxygen in the water, the larger the increase in the corrosion rate (Figure 9).

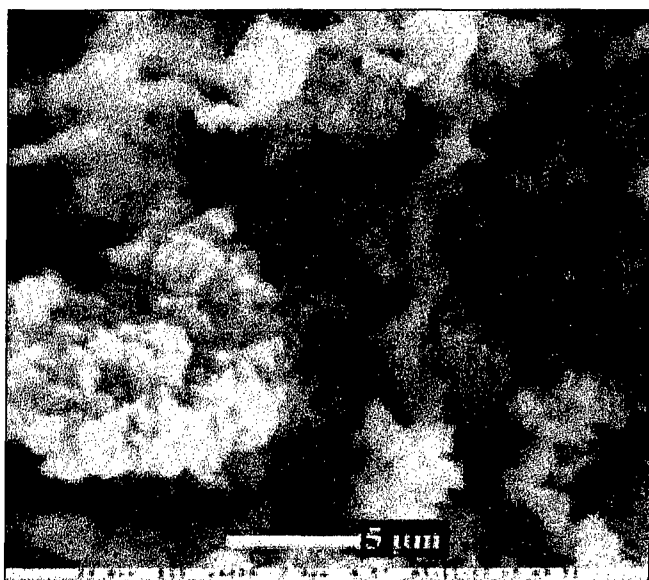
During fill cycles, E_{corr} values within any one exposure condition varied by 50 mV or less. The greatest difference observed was between the bottom row (row 4) and the side rows (rows 1 through 3) in all three exposure conditions (Figure 3). Trends in E_{corr} values are more evident when sorted by row (Figure 4). In each row, the aerobic/aerobic exposure condition had the highest E_{corr} values observed, with the largest E_{corr} value differences (when compared to conditions deoxygenated/aerobic and deoxygenated/deoxygenated) found in rows 1 through 3 (Figures 4[a] through [c]). As discussed previously, coupons in row 4 never fully dried because of the residual water remaining in the bottom of each tank during the drain cycles. Only small differences (<20 mV) were observed between the row 4 E_{corr} values for all exposure conditions (Figure 4[d]). These results suggest that E_{corr} values (during fill cycles) for coupons dried during drain cycles (rows 1 through 3) are more dependent on atmospheric conditions than coupons remaining wet throughout the experiment. As noted earlier, E_{corr} values stabilized during drain cycles after a salt bridge formed between the working and reference electrodes. While these results are interesting, they may not be accurate due to the lack of fully immersed electrodes. Peterson, et al.,¹¹ noted that the impedance of the saltwater film, which bridged working and Ag/AgCl reference electrodes (not fully immersed), was on the same order of magnitude as the internal impedance of the recording instrumentation. The resulting voltage drop across the electrodes was divided between the salt bridge and the instrumentation, resulting in a lower (smaller magnitude) reading. This same trend was observed in the current study during drain cycles (Figures 3 and 4). Peterson, et al., suggest the use of either a very high impedance potentiometer (where the effective in-

Aerobic/Aerobic
Row 4

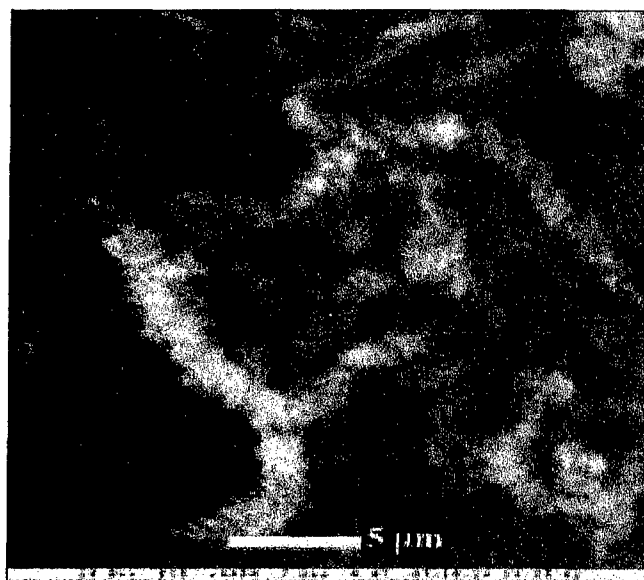
(a)

Aerobic/Aerobic
Row 4

(b)

Deoxygenated/Aerobic
Row 1

(c)

Deoxygenated/Deoxygenated
Row 1

(d)

FIGURE 7. Micrographs of corrosion products from all three exposure conditions from (a) 395 days, (b) 207 days, (c) 146 days, and (d) 395 days. Spiral filamentous bacteria can be seen with and without encrusted iron corrosion products.

strument impedance approaches infinity), resulting in a full (undivided) magnitude reading, or the use of a recording system that has a lower impedance than the salt bridge, which would give no reading or at least a very low reading during drain cycles.

Neither weight loss nor LPR provides an absolute quantification of localized corrosion. Weight loss is an average of material lost from the surface and is best suited for approximations of general corrosion. Weight-

loss measurements do not provide insights into pitting. Intense localized pitting can produce small weight losses. Conversely, the most electrochemically active (corroding) area on a surface dominates linear polarization measurements. Differences in $1/R_p$ values (instantaneous corrosion rates) for side rows in any one experimental condition cannot be readily explained. In the experiments reported here, weight-loss and LPR data indicate the same basic trends and both

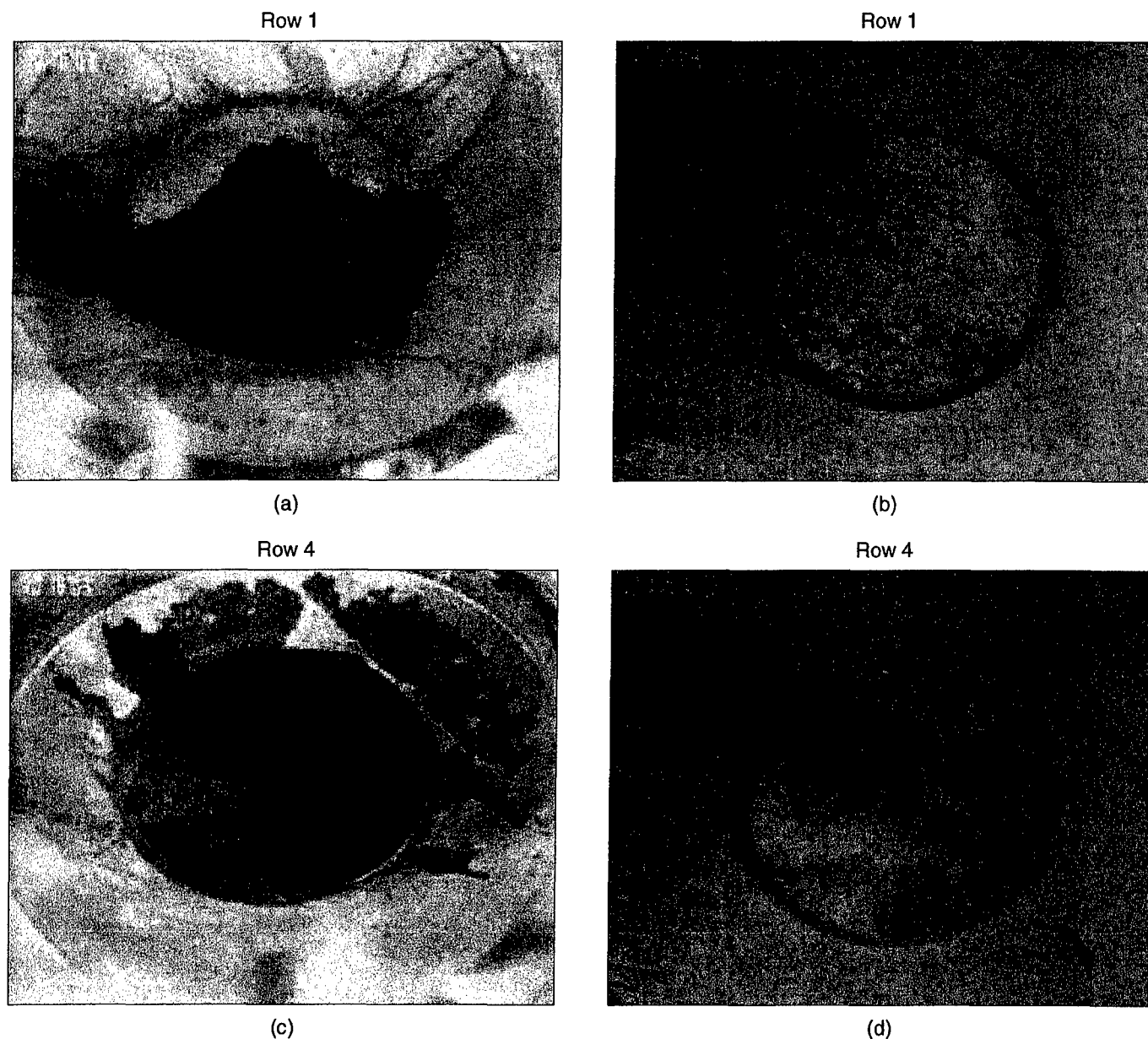


FIGURE 8. Photographs from aerobic/aerobic exposure conditions: ([a] and [c]) before and ([b] and [d]) after acid cleaning from row 1 and row 4 after 170 days' exposure. Prior to cleaning, no difference is observed between the two coupons. However, after cleaning, the row 1 coupon has evidence of severe localized pitting corrosion while the row 4 coupon only has evidence of general uniform corrosion.

can be used for comparing relative corrosion rates. However, pitting could only be described after acid-cleaning and direct examination. XRD, ESEM, and EDS measurements show that it is possible to document precisely the mineralogy, microbiology, and chemical composition of corrosion layers at specific times; however, it is not possible to use those data to predict the type of corrosion, severity, or distribution. In all cases data were influenced by the oxygen concentration at the time of the sample collection.

Despite the presence of bacteria in all surface corrosion products and the measurement of a diverse microbial microflora in the bulk seawater medium, it

is impossible to elaborate on the specific roles/mechanisms of microbiologically influenced corrosion (MIC) in the cycling experiments. Bacterial types were quantified in the seawater at the start of the experiment and after 14 days of stagnation. It is generally recognized that only a small percentage of the natural microflora can be cultured using selective culture media and a single incubation temperature. Furthermore, organisms cultured from the bulk medium cannot be used to approximate the numbers and types of organisms on the surface. No attempt was made to follow the microbial populations on the surface of the coupons. Spatial relationships between the filamentous

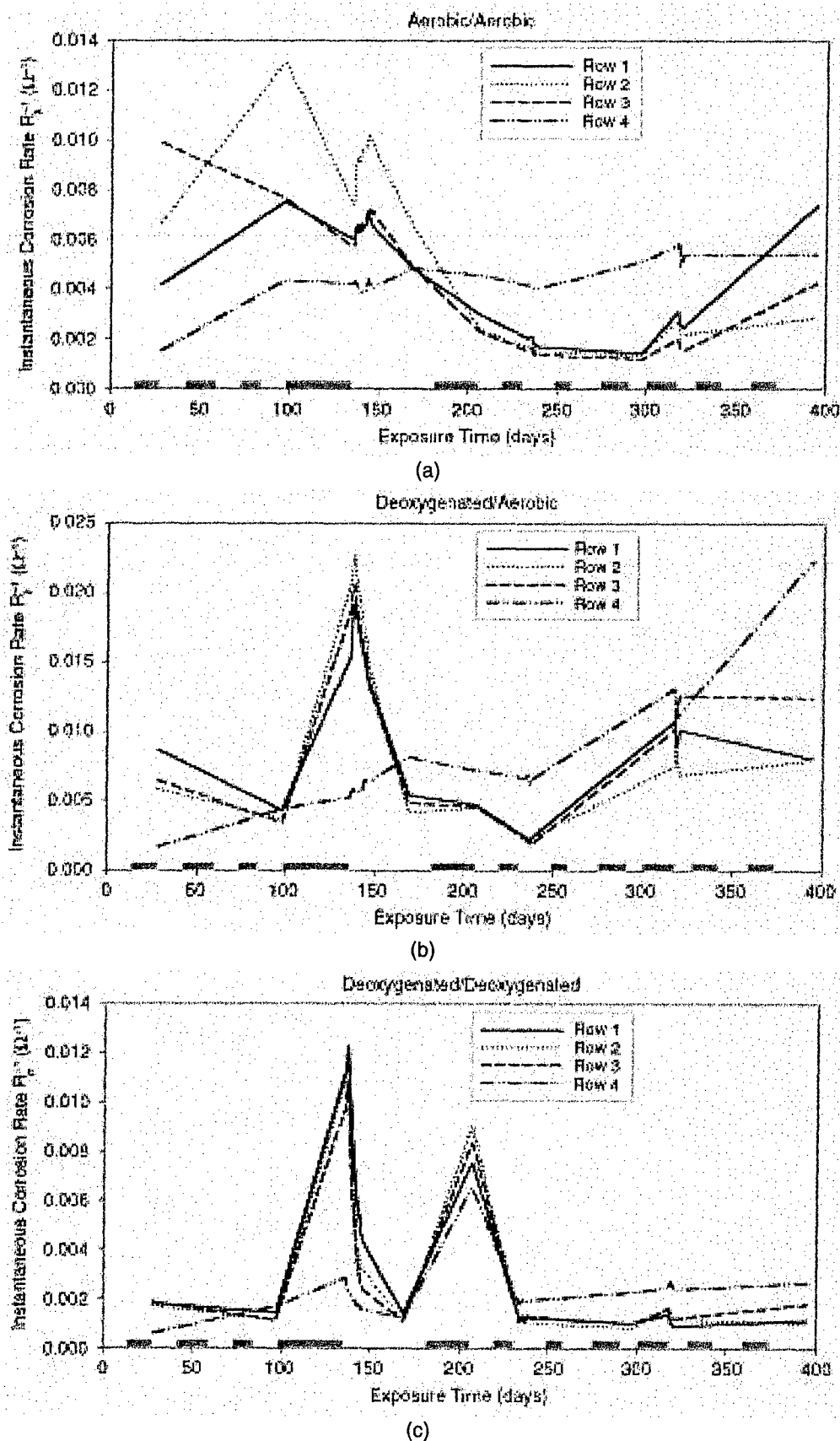


FIGURE 9. Instantaneous corrosion rates ($1/R_p$, Ω^{-1}) of side rows 1 through 3 and bottom row 4 coupons for fill drain exposure conditions over the 395-day exposure: (a) aerobic/aerobic, (b) deoxygenated/aerobic, and (c) deoxygenated/deoxygenated. Shaded areas indicate drain cycle periods.

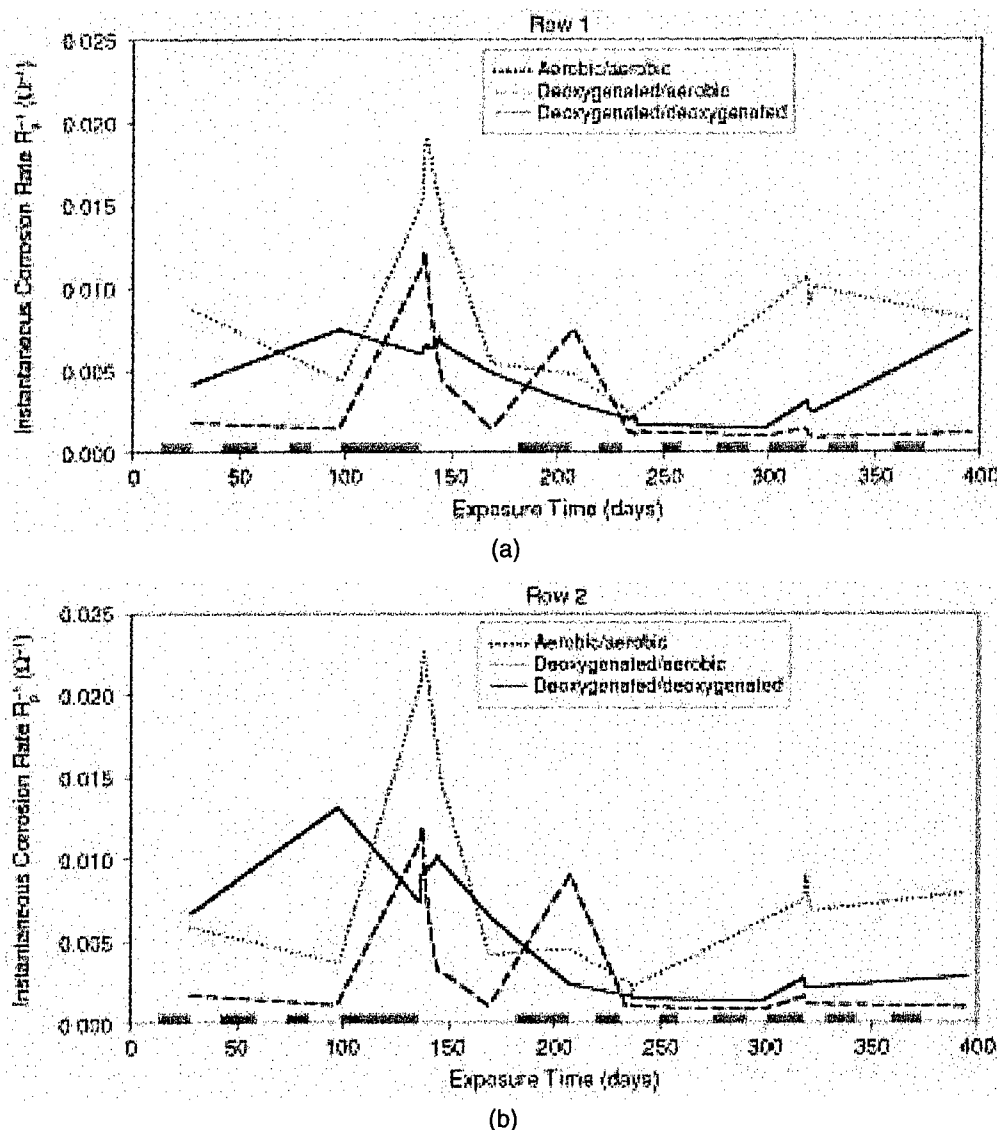


FIGURE 10. Instantaneous corrosion rates ($1/R_p$, Ω^{-1}) for the three fill/drain exposure conditions sorted by row over the 395-day exposure: (a) row 1, (b) row 2, (c) row 3, and (d) row 4. Shaded areas indicate drain cycle periods.

bacteria and corrosion products (Figure 7) cannot be interpreted as MIC because bacteria are attracted to anodic sites on ferrous materials exposed in seawater.¹² In previous experiments, Lee, et al.,³⁻⁴ demonstrated that SRB were responsible for the corrosion of carbon steel exposed to totally anaerobic seawater for one year. The corrosion product was predominantly mackinawite, a mineralogical fingerprint for SRB-influenced corrosion of carbon steel.¹³ In the experiments described in this paper, dissolved sulfides increased in all experimental conditions (Table 3) and SRB were cultured from waters in two of the three tanks. It is interesting to note that SRB could not be cultured from the natural seawater at the time of collection or from deoxygenated water with an aerobic headspace after 14 days of a fill cycle using Postgate medium B (Table 3). The absence of SRB growth in Postgate medium B cannot be interpreted as an ab-

sence of SRB in the seawater, but only as an inability to grow the organisms in a particular medium. However, the oxygen level in the deoxygenated/aerobic condition was highest at the time of collection (Day 98), as shown in Figure 2(a), which may account for the lack of culturable SRB. Only trace amounts of sulfides were identified in the corrosion products of the deoxygenated/deoxygenated tank. Periods of deoxygenation could increase localized corrosion resulting from the activities of naturally occurring microaerophilic, facultative, or obligate anaerobic bacteria. Seawater contains 2 g/L sulfate that can be reduced to sulfide by SRB in the absence of oxygen. Deoxygenation can also result in putrefaction, the anaerobic breakdown of sulfur-rich proteins, and levels of sulfides will not be limited to the sulfate concentration in the seawater. Sulfide reacts with iron oxide, formed in the atmosphere or in oxygenated seawater, to produce

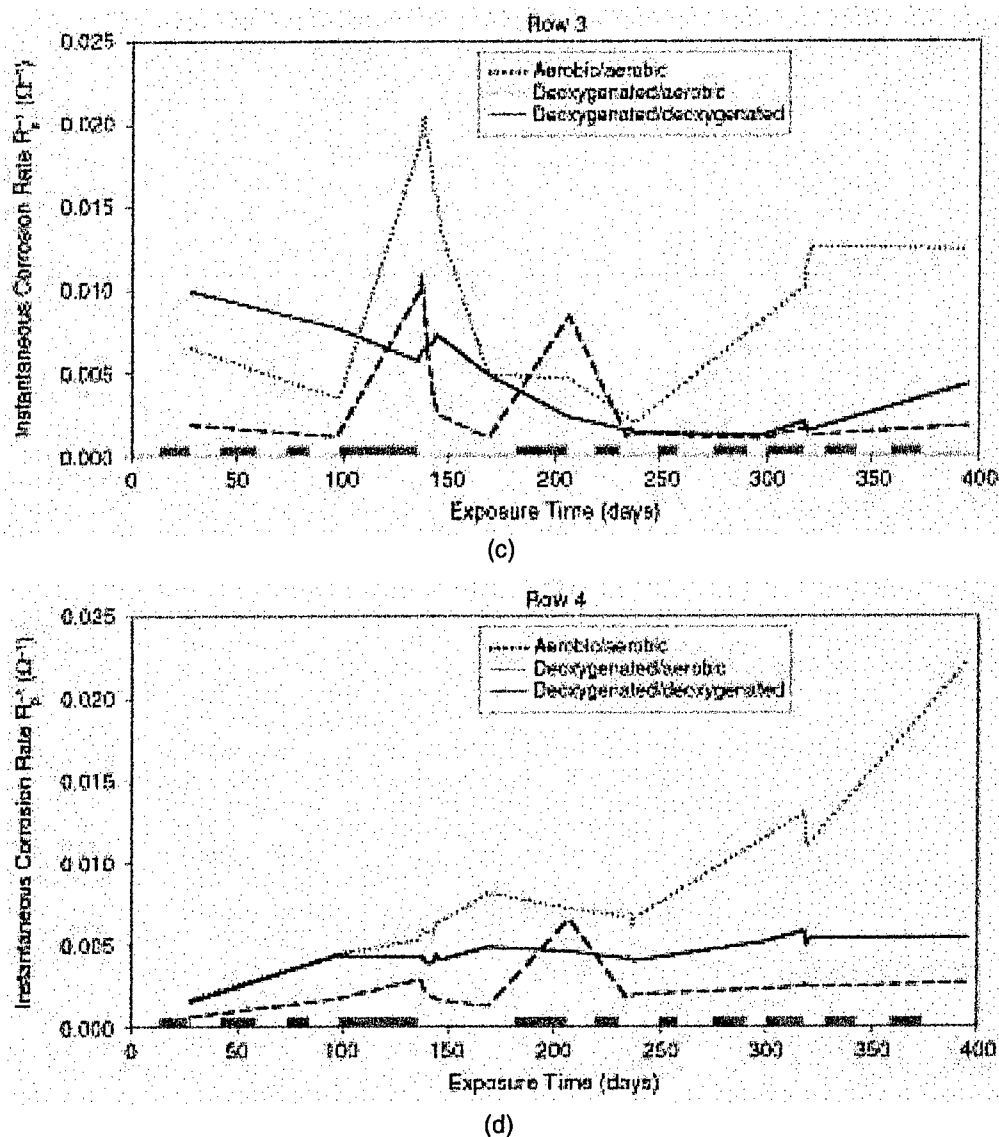


FIGURE 10 (continued). Instantaneous corrosion rates ($1/R_p$, Ω^{-1}) for the three fill/drain exposure conditions sorted by row over the 395-day exposure: (a) row 1, (b) row 2, (c) row 3, and (d) row 4. Shaded areas indicate drain cycle periods.

a nontenacious iron sulfide layer that can be removed with stress or converted back to an oxide by the introduction of oxygen. In either case the sulfide layer is not uniformly removed or oxidized, creating adjacent anodic and cathodic regions and aggressive corrosion. Again, these "snapshots" of the microbial population in the bulk seawater are interesting, but cannot be interpreted as to their impact on the corrosion. Desiccation during the drain cycles may have prevented the establishment of a biofilm and the conditions for MIC.

Hamilton⁸ recently proposed a model for MIC in which he concluded all mechanisms involved a process of electron transfers from the base metal to oxygen as the ultimate electron acceptor through a series of coupled reactions. The specific coupled reactions varied with the mechanism and causative organism. In the case of SRB, sulfate, an intermediate electron acceptor, is reduced to sulfide that reacts with iron

to form a corrosion product that ultimately transfers electrons to oxygen. Consistent with that model, most reported cases of SRB-induced corrosion of carbon steel in marine waters are in environments with some DO in the bulk medium.^{9,14} Lee, et al.,³⁻⁴ recently demonstrated that oxygen was not required for localized corrosion of carbon steel exposed to seawater. In fact, they demonstrated more aggressive, localized corrosion of carbon steel in totally anaerobic stagnant natural seawater than in oxygenated stagnant natural seawater. They further demonstrated that the introduction of oxygen to the totally anaerobic stagnant tank caused an immediate increase in weight loss and instantaneous corrosion rate. The $1/R_p$ data from those stagnant experiments are compared with the fill/drain cycling data presented in this paper in Figure 12. Stagnant aerobic conditions had the lowest corrosion rates while the bottom row of the stagnant

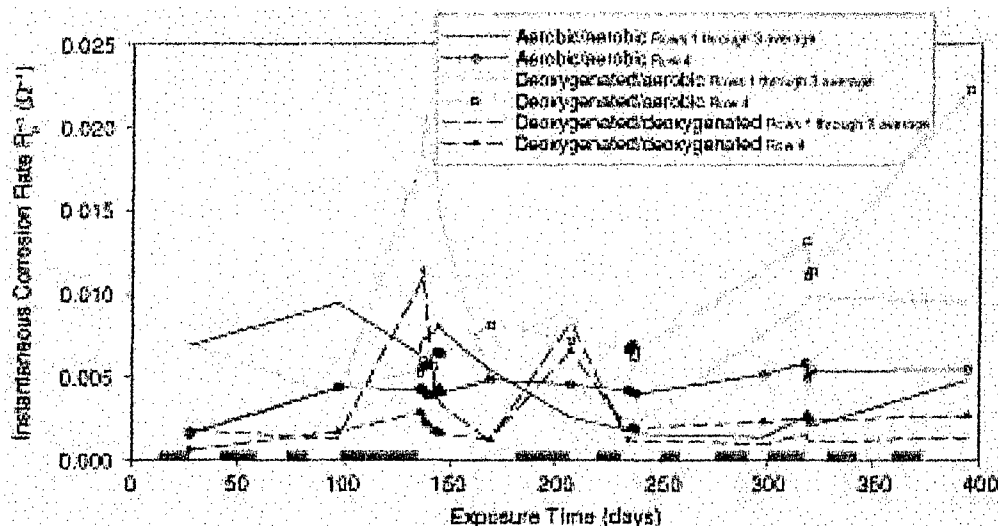


FIGURE 11. Instantaneous corrosion rates ($1/R_p$, Ω^{-1}) of side (average of rows 1, 2, and 3) and bottom row 4 coupons for the three fill/drain conditions for the 395-day exposure. Shaded areas indicate drain cycle periods.

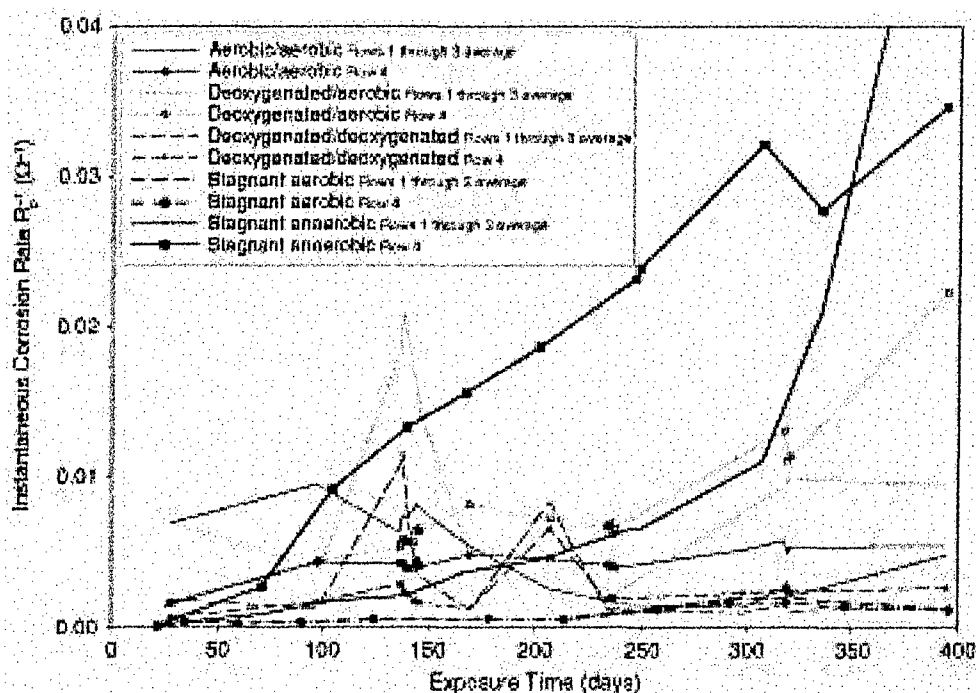


FIGURE 12. Instantaneous corrosion rates ($1/R_p$, Ω^{-1}) of side (average of rows 1, 2, and 3) and bottom row 4 coupons for the three fill/drain conditions for the 395-day exposure (Figure 15) in comparison to stagnant aerobic and stagnant anaerobic conditions. Stagnant aerobic conditions had the lowest corrosion rates, while the bottom row of the stagnant anaerobic case had the highest.

anaerobic case had the largest (until the end of the exposure period, at which time the side rows had the largest). The $1/R_p$ data from all cycling experiments were intermediate between those extremes.

CONCLUSIONS

❖ Experiments described in this paper demonstrate the potential application of deoxygenation as a corro-

sion control measure for unprotected carbon steel ballast tanks. However, they also demonstrate the impracticability of such an approach to corrosion control.

❖ Any attempts to use deoxygenation as a corrosion control measure will have to consider both the consumption of oxygen by aerobic respiration and corrosion reactions, as well as the introduction of oxygen from the atmosphere.

❖ Introduction of oxygen into an anaerobic/hypoxic system resulted in an increase in the corrosion rate and severity. Neither can be predicted based on the concentration of introduced oxygen.

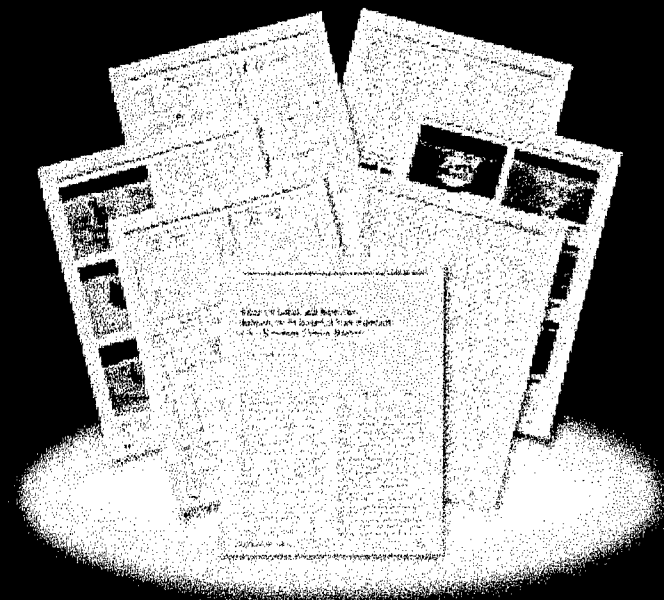
ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research Program element 0601153N (6.1 Research Program) and the University of Maryland. XRD data were collected at the MicroBeam Laboratory in the Department of Geology and Geophysics at the University of New Orleans, New Orleans, Louisiana. The authors would also like to thank P. Glandt, S. Dembek, and B. Naley for all their help during the fabrication of the system and periodic data collection. NRL Publication Number NRL/JA/7303/--05-5/35.

REFERENCES

1. M.N. Tamburri, K. Wasson, M. Matsuda, *Biol. Conserv.* 103, 3 (2002): p. 331-341.
2. M. Matsuda, S. Kobayashi, H. Miyuki, S. Yosida, "An Anticorrosion Method for Ballast Tanks Using Nitrogen Gas," Report of Research and Development to the Ship and Ocean Foundation (Japan), October 1999.
3. J.S. Lee, R.I. Ray, E.J. Lemieux, A.U. Falster, B.J. Little, *Biofouling* 20, 4/5 (2004): p. 237-247.
4. J.S. Lee, R.I. Ray, E.J. Lemieux, B.J. Little, "An Evaluation of Carbon Steel Corrosion Under Stagnant Seawater Conditions," *CORROSION/2004*, paper no. 04595 (Houston, TX: NACE International, 2004).
5. J.A. Hardy, J.L. Bown, *Corrosion* 42, 12 (1984): p. 650-654.
6. W.C. Lee, Z. Lewandowski, S. Okabe, W.G. Characklis, R. Avci, *Biofouling* 7 (1993): p. 197-216.
7. W.C. Lee, Z. Lewandowski, M. Morrison, W.G. Characklis, R. Avci, P.H. Nielsen, *Biofouling* 7 (1993): p. 217-239.
8. W.A. Hamilton, *Biofouling* 19, 1 (2003): p. 65-76.
9. W.A. Hamilton, S. Maxwell, "Biological and Corrosion Activities of Sulphate-Reducing Bacteria Within Natural biofilms," in *Biologically Induced Corrosion*, ed. S.C. Dexter (Houston, TX: NACE, 1986), p. 131-136.
10. L.S. Clesceri, A.E. Greenberg, A.D. Easton, "Sulfide 4500 D Methylene Blue Method," in *Standard Methods for the Examination of Water and Wastewater* (Washington, DC: American Public Health Association, 1998), p. 4/165.
11. M.H. Peterson, K.E. Lucas, E.A. Hogan, A.I. Kaznoff, "Reference Half-Cells for the Ocean Environment," *CORROSION/2001*, paper no. 01301 (Houston, TX: NACE, 2001).
12. B.J. Little, R.I. Ray, R.K. Pope, M.J. Franklin, D.C. White, "Spatial and Temporal Relationships Between Localised Corrosion and Bacterial Activity on Iron-Containing Substrata," *Microbial Corrosion: 4th Int. EFC Workshop*, vol. 29 (London, U.K.: Institute of Materials, 1999), p. 21-35.
13. M.B. McNeil, J.M. Jones, B.J. Little, "Mineralogical Fingerprints for Corrosion Process Induced by Sulfate-Reducing Bacteria," *CORROSION/91*, paper no. 580 (Houston, TX: NACE, 1991).
14. P.F. Sanders, W.A. Hamilton, "Biological and Corrosion Activities of Sulphate-Reducing Bacteria in Industrial Process Plant," in *Biologically Induced Corrosion*, ed. S.C. Dexter (Houston, TX: NACE, 1986), p. 47-68.

Spotlight your business with *CORROSION* ads, articles, and cover reprints!



Your hard-copy reprints can be customized to place you in the spotlight.

Reprints are excellent for:

- investor packets
- media kits
- trade show handouts
- direct mail pieces
- thesis paper reproductions

Add third-party credibility to sales literature enhancing your company's image.

For more information about branded *Corrosion* reprints and rates, contact Stacia Brooks at 281/228-0219, e-mail: stacia.brooks@nace.org, or visit www.nace.org.

THE JOURNAL OF SCIENCE AND ENGINEERING
CORROSION